Material Properties of Bi-Modal
Epoxy Networks

Stephen J. MacKenzie
Thomas J. Mulkern
Nora C. Beck Tan

20010426 062

Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5066

ARL-TR-2413   March 2001

Material Properties of Bi-Modal Epoxy Networks

Stephen J. MacKenzie
University of Delaware

Thomas J. Mulkern
Nora C. Beck Tan
Weapons & Materials Research Directorate, ARL

Abstract

The necessity for epoxies in new technologies is overwhelming. For these epoxies to perform at their maximum capabilities, both high strength and toughness must be in the list of mechanical properties. This is where bi-modal networks become important. Their combinations of both long- and short-chain cross linkers vary the cross-link density of the epoxy and thus improve the toughness. Here, a study was done to see if these bi-modal networks increase toughness without loss in modulus. Through the use of the differential scanning calorimeter to find the glass transition temperature, the dynamic mechanical analyzer to find the storage modulus, and the Izod impact machine to find the impact strength, we can make a conclusion whether these networks really work. In the beginning, the results seemed to be what we had hoped for, that is, the decrease in cross-link density did improve the impact strength; however, the storage modulus also decreased with a decrease in cross-link density. Finally, the conclusion can be stated that the bi-modal network does increase the toughness of this system but with a loss in modulus.

ACKNOWLEDGMENTS

INTENTIONALLY LEFT BLANK

Contents

Tables

1. Introduction and Literature Survey

The use of epoxies in today's technologies has become an important part of manufacturing quality goods. Epoxy resins were first offered in 1946 and are now used in a wide variety of industries. Nearly half of all epoxies sold in the United States go toward protective coatings, while the remainder is used in structural applications such as laminates and composites, tooling, molding, casting, electronics, construction, bonding and adhesives [1]. The characteristics of epoxy resins are high chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, flexibility, good electrical properties, and the ability to be processed in a variety of conditions [1]. These characteristics, along with a long service life, make epoxies a necessity in the future growth of new technologies.

The identifying characteristics of epoxy resins are the presence of a three-member ring known as the epoxide group. A long aliphatic, cyclo-aliphatic, or aromatic backbone connects two epoxide rings. The capability of these rings to react with curing agents yields insoluble and intractable thermoset network polymers. Epichlorohydrin and bisphenol A-derived resins are the most widely used epoxy resins. The outstanding performance characteristics of the resins are conveyed by the bisphenol A moiety (toughness, rigidity, and elevated temperature performance), the ether linkages (chemical resistance), and the hydroxyl and epoxy groups (adhesive properties and formulation latitude) [2].

An epoxy network is formed when epoxide groups are reacted with a diamine cross-linking agent in the stoichiometric ratio of 2:1 epoxies per cross linker. The mechanical properties of epoxies depend on their network structure and cross-link density. For example, in a cured epoxy resin of fixed chemistry, the strength and modulus of the resin increase as the cross-link density of the network increases, while the fracture toughness of the resin decreases with increasing cross-link density [3]. Toughness is related to how the material reacts to stress concentrations such as sharp cracks [4]. Another property is the glass transition temperature of the epoxy network, which has an effect on the strength and modulus as well as the toughness. The glass transition temperature, unique for each epoxy system, is the temperature where the material starts to exhibit rubber-like characteristics, for example, an increased toughness and loss of modulus [5]. The glass transition temperature is also affected by the cross-link density; that is, as the cross-link density increases, so does the glass transition temperature; therefore, the modulus and the toughness of the material are directly affected by the glass transition temperature of the epoxy [5].

1

Since both high modulus and high fracture toughness are required of structural materials, sacrifices in strength and toughness generally must be made in order to design useful epoxies. (The term toughness refers to a material with both high strength and high ductility in which strength is the amount of energy required to produce permanent deformation of the material [3]). This is where the properties of bi-modal networks interact. A bi-modal network is an epoxy network that uses both short- and long-chain cross linkers instead of one or the other. This bi-modal distribution of cross-linker chain length will vary the cross-link density and may produce a material with both strength and toughness [6].

Previous studies of the mechanical properties of bi-modal networks have shown that the varying cross-link density of bi-modal networks leads to superior mechanical properties [7]. A study by Madkour and Hamdi, done at the Department of Chemistry at Helwan University in Cairo, Egypt, shows that elastomers cured with sulfur and polyquinine cross linkers of greater lengths (a lower cross-link density) produce a bi-modal network with exceptional mechanical properties [7]. These properties include high strength and toughness. When stress-strain measurements were performed on these elastomers with two cross-linking systems, the maximum Young's modulus values were obtained after three days of continuing aging time, when the maximum bi-modal chain length distribution took place [7]. This maximum bi-modal chain length distribution is when the polymer exhibits the most amount of varying cross-link densities and thus as an even distribution of both long- and short-chain cross linkers throughout the polymer system.

Mechanical property studies done on single modal networks show that an increase in cross-link density increases stiffness and decreases the elastic modulus [8]. Thus, a decrease in cross-link density would decrease stiffness and increase the elastic modulus. At the *Institut National des Sciences Appliquees de Lyon* in Villeurbanne Cedex, France, a study was done on the influence of chain flexibility and cross-link density on mechanical properties of epoxy-amine networks. The amount of chain flexibility is in direct proportion to the length between the epoxide rings, and the amount of cross-link density is based on the length of the cross-linking agents. The final conclusion was that two main factors affected the toughness of epoxy networks: chain flexibility and cross-link density [9].

A joint study between the Department of Chemistry at Cairo University and the Department of Chemistry and Polymer Research Center at the University of Cincinnati shows that elastomers with high functionality cross links, that is, two distinct lengths, can be viewed as bi-modal networks. Studies done on these elastomers show that both short and long chains are present and this presence of a large number of short chains gives rise to a remarkably high modulus [10].

2

Another way of toughening epoxies is to induce elastic rubber particles into the epoxy matrix. This is a more conventional method than the use of bi-modal networks for toughening materials. J.F. Hwang and others from the Center for Polymer Science and Engineering at Lehigh University conducted a study of the structure-property relationships in rubber-toughened epoxies. They concluded that the structure was two phases consisting of spherical rubber particles dispersed in the epoxy matrix. This rubber toughening increased impact strength, plain strain fracture toughness, and fracture energy, while Young's modulus and yield strength decreased slightly with rubber incorporation [11]. (Plain strain fracture toughness is a test done on a narrow strip of sample in which the sample is compressed by narrow plates until the sample fractures.) The result is a measure of the toughness of the material.

At the Institute of Materials Science and Technology in Mar del Plata, Argentina, C.I. Callo and others performed a similar study using rubber-toughened hybrid epoxies. His study was conducted with diglycidyl ethers of bisphenol A (DGEBA) epoxy and carboxly terminated butadiene acrylo-nitrile (CTBN) rubber particles to form the network. Results were similar to those of Hwang and showed that introducing a rubber phase into the epoxy matrix increases fracture toughness and lowers flexural modulus and yield stress [12]. Rubber toughening sounds very promising, but there are some serious disadvantages to inducing rubber particles into an epoxy matrix. One is that as the material toughens, the modulus will decrease, which happens because more rubber particles that have lower glass transition temperature and modulus are added. Another problem is the bonding characteristics between the rubber and the epoxy; some epoxies will not bond with the particles, leaving a material with inherent weak spots. The final problem will occur mostly in industrial applications when complex composite pieces need to be manufactured. Here, the rubber particles are excluded by the tightly woven fabrics during processing, leaving all the rubber particles on one side of the fabric and the epoxy on the other [13]. This is when the bi-modal epoxy networks become important; they do not exhibit the last two problems associated with rubber-toughened epoxies, and after extensive research, it is possible that they will not exhibit the first problem.

In this study, we hypothesize that mixing two different lengths of cross linkers (each with the same chemistry) with the epoxy will directly induce the bi-modal network and thus toughen the material. This method is unique because in past studies, the bi-modal network was always obtained by varying the extent of curing by mixing two different cross linkers with varying chemistry together with the epoxy, or the epoxy was toughened by the introduction of rubber particles. The introduction of the long-chain cross linkers is in itself like rubber toughening because epoxy made with only the long-chain cross linkers is very rubber like. Therefore, one can conclude that the bi-modal epoxy network is like a pseudo rubber-toughened epoxy without any of the manufacturing problems. If successful, this study will show that a directly induced bi-modal network will

produce both strength and toughness in an epoxy network and produce better results than rubber-toughened epoxies. Past experiments show that bi-modal networks have enhanced mechanical properties on other polymer systems, but no one has proved that it will do the same for a directly induced epoxy system.

2. Experimental Background

In order to conduct this study of the mechanical properties of bi-modal networks, several experiments were performed in a specified order. The glass transition temperature was measured first with a differential scanning calorimeter (DSC); then the elasticity and modulus were measured with a dynamic mechanical analyzer (DMA). The final study was an impact study with an Izod impact machine.

The glass transition temperature is the temperature at which the material begins to exhibit liquid properties. This transformation occurs when the molecules' translational motion starts to occur and the thermal motion starts to increase [14]. The increase in thermal motion can be measured with a DSC in the form of heat capacity. A DSC is an isoperibol calorimeter, which means that the environment is kept at a constant temperature, while the temperature changes with time (heating rate) are governed by the thermal resistance between calorimeter and surroundings [14]. The difference in measured heats is between the sample and a reference, which are both present inside the DSC and are heated at the same rate. A reference is just an empty aluminum sample holder with no sample present. The precision of a DSC is quite good. A typical sample weighs 20 mg and shows a heat capacity of 50 mJ/°K, that is, the precision is ±0.001 J, or a measured precision of 20%. This is an acceptable value for heat capacity that changes slowly with temperature [14]. The glass transition temperature will be measured for all samples, and those that present a glass transition temperature of 30° or more above room temperature will be studied further. These samples will be used because they are all "glassy" at room temperature and if samples that have glass transition temperatures below room temperature were used, then biased results would occur. Figure 1 is a sample curve of the results obtained from the DSC; notice the onset lines used to find the glass transition temperature.

A DMA will be used on the glassy materials to study the modulus and the elasticity. The modulus is a constant for each material that relates stress to strain, in which the stress is directly proportional to the strain and is independent of the strain rate, that is, perfect elasticity. This perfect elasticity is an ideal behavior described by Newton's law. The idealized laws cannot describe the behavior of matter if the ratios of stress to strain or of stress to rate of strain are not constant.

4

Plastic deformation is a common example of such non-ideal behavior. It occurs for solids if the elastic limit is exceeded and irreversible deformation takes place [15]. The DMA is not the only piece of equipment that will analyze a material and calculate the modulus and the elasticity. One such common method is the tensile test, in which the material is subjected to a continually increasing uniaxial tensile force while observations are made of the elongation of the specimen. From these data, a curve of the stress-strain relationship is produced. The only problem with this method is that a large amount of material is required to do these tests, compared to the few milligrams of material needed to run a DSC experiment. The DMA senses and quantifies all changes in the degree of molecular motion in a material and gives the elastic storage modulus (log of Young's modulus) and damping (tangent of the deformation angle) over its full temperature and frequency range. A damping peak occurs in sympathy with each motional change that signals an increase the dissipation of energy [14]. Figure 2 is an example of a typical DMA result curve. Notice how similar it is to a DSC curve except that modulus is recorded as a function of time.
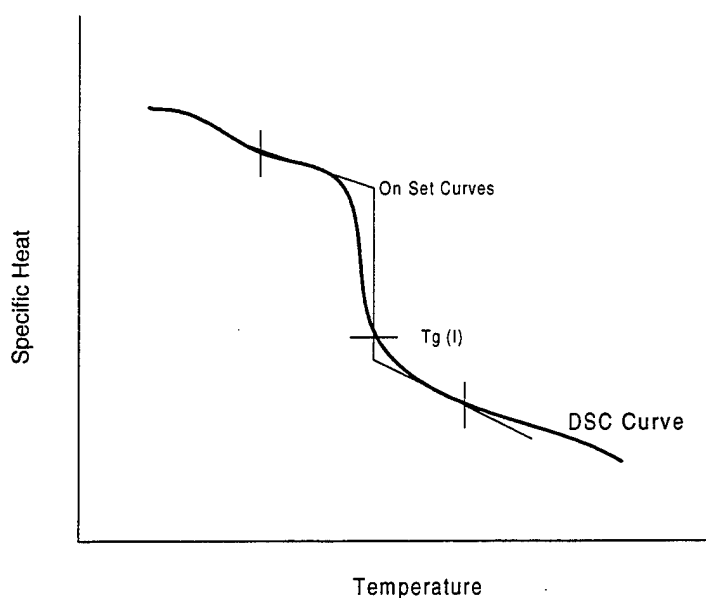
Figure 1. Sample DSC Curve. (Notice how the onset curves are used to find the T_g glass transition temperature.)

The final study will involve the use of an Izod impact tester (American Standard for Testing Materials [ASTM] D256) in order to find the impact strength of the material. The impact strength or impact energy is the energy necessary to fracture a standard test piece with an impact load [3]. This type of experiment is used to determine the tendency of a material to behave in a brittle manner and will also detect differences between materials, which are not observable in a tension experiment. Three experiments must be done with the Izod, one at room temperature, one at a temperature that is 200°C below the lowest glass transition

temperature, and one at set incremented temperature from each of the samples' respective glass transition temperatures. The reason behind the latter two experiments is to remove any effects that the different sample glass transition temperatures have on the toughness. As the samples' glass transition temperature decreases, the material becomes more rubbery, and thus, its toughness increases. By testing each sample at different temperatures, the effects of the glass transition are removed, and each sample can be compared to the others without biased results.
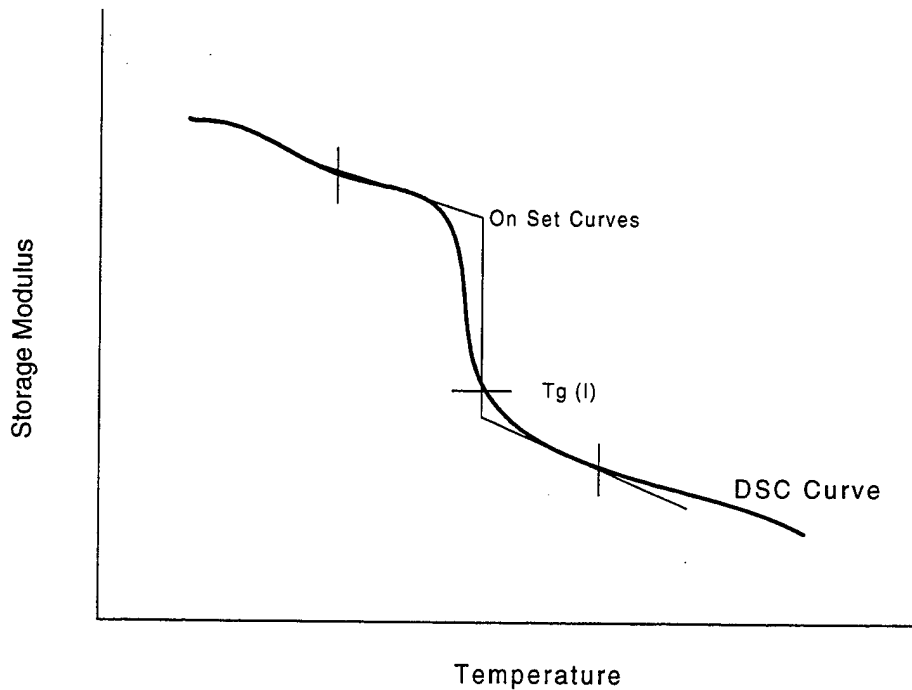
Figure 2. Sample DMA Curve (very similar to the DSC curve).

There are three factors that contribute to a brittle fracture: a triaxial state of stress, a low temperature, and a high strain rate of rapid rate of loading. All three factors do not have to be present at the same time to produce brittle failure [11]. The Izod experiment uses the principle of turning kinetic energy into potential energy through the use of a swinging pendulum. The principal measurement from the impact experiment is the energy absorbed in fracturing the specimen and is frequently used for quality control and material acceptance purposes [4].

3. Project Objectives

The purpose of this research is to investigate whether a bi-modal epoxy network will have improved strength and toughness relative to a similar regular epoxy network. An epoxy resin and two cross linkers of identical chemistry but different molecular weight were chosen and a series of bi-modal networks was prepared from them. In the series of bi-modal networks, the cross-link density of the epoxy was varied by changing the mole ratios of the two cross linkers, while keeping the total mole ratio of epoxy to cross linker at 2:1. The experiments included DSC to find the glass transition, followed by DMA and Izod experiments to find the modulus and impact strength, respectively. The toughness of the material is characterized by the impact strength, since a direct correlation can be drawn that relates impact strength to toughness. That is, as the impact strength increases, so does the toughness.

4. Description of Equipment

To complete any research project, different types of equipment are employed to perform the tedious tasks of running experiments. In this particular project, three major pieces of equipment were used to acquire knowledge of the material properties' bi-modal networks: a DSC, a DMA, and an Izod impact machine. The DSC was the first piece of equipment used to analyze the glass transition temperature of each sample. This machine requires only a few milligrams of material, which are placed inside an aluminum pan and sealed. This pan is then placed inside the DSC, along with an empty reference pan. Here, the DSC measures the heat difference between the sample and a blank reference while increasing the temperature at a constant rate. The data are stored in a computer and plotted against temperature to find the glass transition. Figure 3 shows the DSC setup; notice the nitrogen and helium tanks that are used to purge the DSC cell to ensure a constant convection of heat inside the cell. Notice the RCS (refrigeration cooling system), which allows one to cool a sample to -80° C.

The next piece of equipment is the DMA, which is used to find the storage and loss modulus of a material. The DMA is very similar to the DSC in that it measures mechanical properties as a function of temperature, but the DSC does not impose stress. The sample used is a 21-mm by 5-mm by 1-mm strip of material that is placed between a pair of vice grips. The sample is subjected to a cyclical pull-relax force as a function of temperature; that is, the material is stretched with a specified force. The result is the storage modulus of the material as a function of temperature. Unlike the DSC, the DMA is capable of cooling a

sample to –180° C with liquid nitrogen. Figure 4 shows a DMA setup; notice that there is no need for the purging gas.
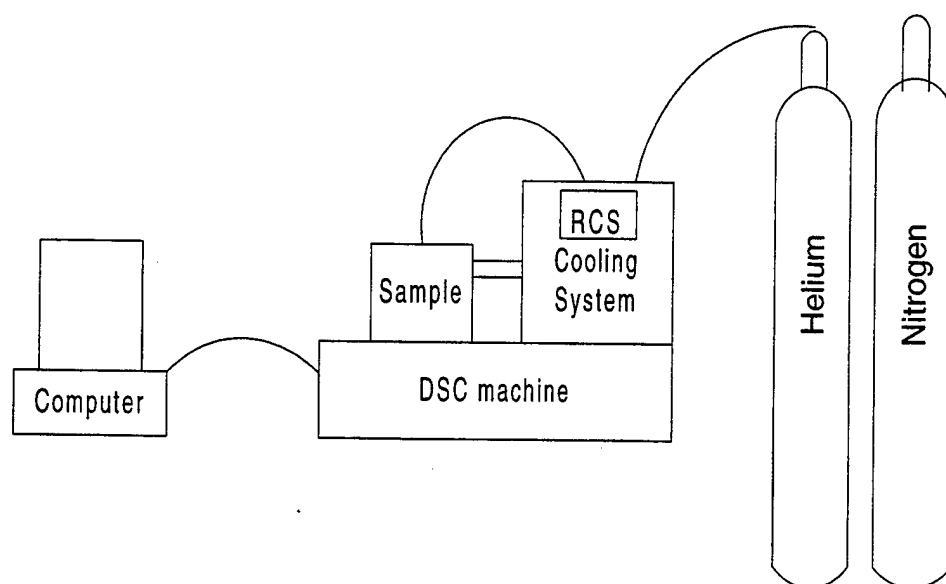
Figure 3. A Typical DSC Setup.
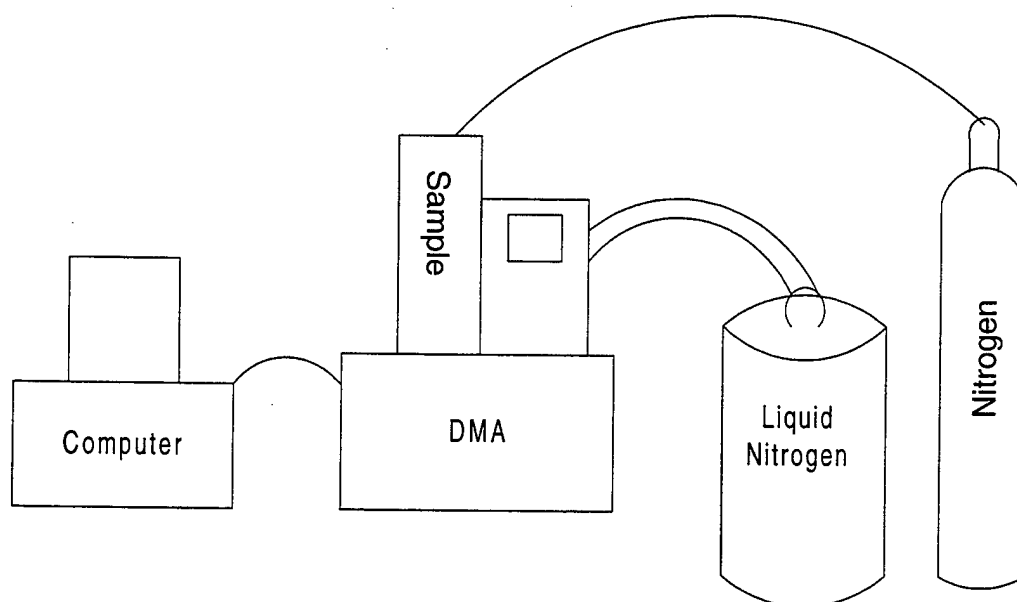
Figure 4. A Typical DMA Setup.

The Izod impact machine was used to determine the impact strength of a piece of material. The sample is struck with a 2-pound hammer and the amount of energy lost is determined. The principle of turning potential energy into kinetic energy makes this piece of equipment easy to operate. The most difficult part is cutting (i.e., "machining") the sample to the correct specifications required by the ASTM D256 standard; this required the aid of an expert machinist. The readings from the experiment must be converted to impact strengths and corrected for friction losses with the equations provided in the ASTM D256 standard. Figure 5 shows a schematic of the Izod machine; notice its simplicity.
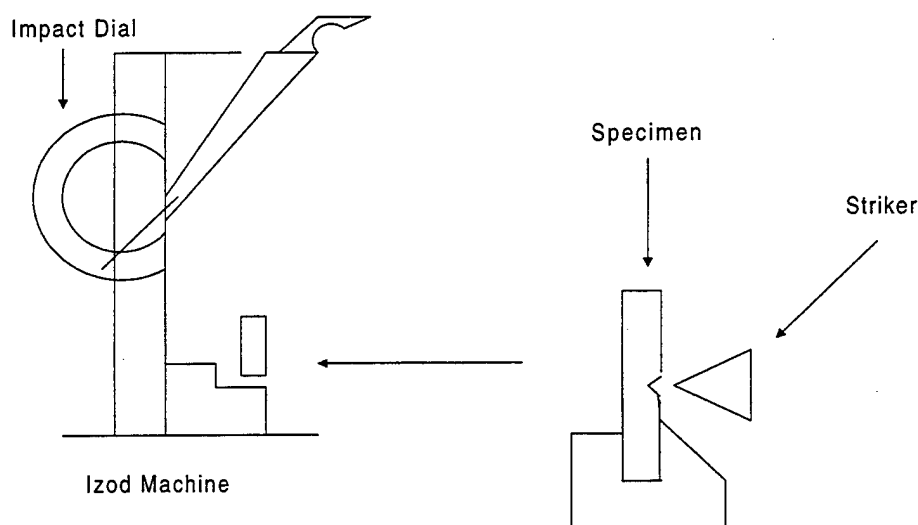
Figure 5. The Notched Izod Impact Machine.

The final piece of equipment used was the tensile mold that was used in the preparation of the Izod impact samples and the DMA samples. The mold was machined from a solid piece of aluminum that had a removable back in order to free the cured samples. The dimensions of the mold are 3.5 inches by 2.5 inches by 1.0 inch; Figure 6 shows a diagram of the mold.
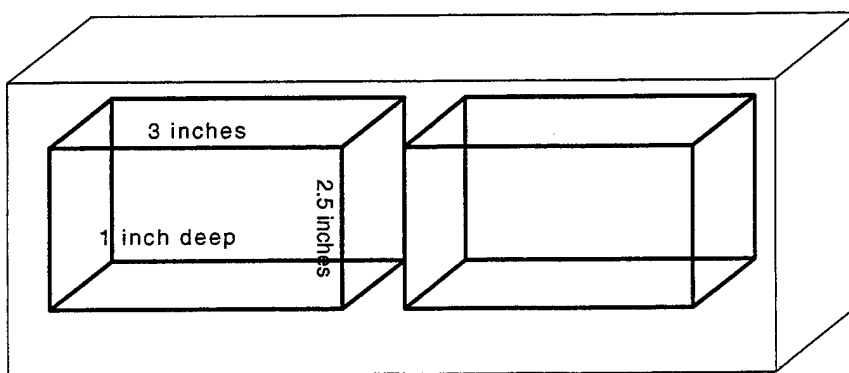
Figure 6. A 3-D Diagram of the Mold Used in Making the DMA and Izod Samples.

Other, less significant pieces of equipment were also used: a vacuum oven to remove the bubbles from the molds. A slow speed saw used to cut the very thin samples necessary for the DMA; a hack saw and miter box to cut larger samples for the Izod. The combination of these lesser pieces of equipment with the three main pieces led to the successful completion of this project. A list of each piece of equipment, the model number, and manufacturer follows:

1. DSC – TA Instruments Model 2920 modulated

2. DMA – TA Instruments Model 2980

3. Izod impact tester – Testing Machines, Inc., Model 43-1

4. Vacuum oven – VWR[1] Scientific

5. Slow speed saw – Buehler Isomet

---

5. Experimental Methods

The raw materials used in these experiments were EPON[1] 828 epoxies supplied by Shell Chemical Corporation, and the cross linkers used were D-230 and D-2000 Jeffamines from Huntsman Chemical Corporation. The 230 and 2000 refer to the average molecular weight of the cross linkers. Three experiments will be performed on the final bi-modal networks: a DSC experiment to find the glass transition temperature of each sample, a DMA experiment to find the modulus, and an Izod experiment to determine the impact strength.

To complete this research in a timely and orderly fashion, fixed procedures were followed. These methods will not only accomplish the desired goals but will also promote success and bring about quality work. Before doing any research on epoxy networks, one must first examine all the different epoxy systems that can be used to form the network. The characteristics that one looks for are the following: the epoxy and cross linker must be reactive with each other, they must be readily available, and when the network is formed, an even distribution of cross-link density must be observed. The determination of an even distribution of cross-link density is commonly done by small angle X-ray diffraction. These characteristics were found for a number of systems, including the Br-DGEBA epoxy/Jeffamine system, which was too difficult to study because of high melting point of the epoxy, and the EPON 828/Jeffamine system; the latter system was chosen because it was easier to study.

To ensure that every epoxy reacts with every cross linker, one must mix the two chemicals together in a 2:1 mole ratio of epoxy to cross linker. These mole ratios

---

[1] Not an acronym

10

were maintained for each cross-linker mixture, and their subsequent weight fractions were calculated (see Appendix A). Then, 5- to 10-gram mixtures were made for each of the cross linker ratios (see Appendix B) in 0.5-cm aluminum pans. These pans were then placed in a vacuum oven drawing (i.e., "pulling") 15 inches mercury for 1 hour to remove any bubbles. A final vacuum of 29.5 inches mercury was pulled for 3 hours to remove the few remaining bubbles before curing. The cure cycle for this system consists of a pre-cure for 2 hours at 80° C, followed by a post-cure at 125° C for 8 hours. After curing, the pans were removed and a 10- to 20-mg sample was taken from the center of each sample. Table 1 shows the calculated epoxy and cross-linker weight percents used in the mixing of the samples. The numbers represent the amount of epoxy and cross linkers that must be added to ensure the correct mole ratio of epoxy to short to long cross linkers.

Table 1. Calculated Table of Epoxy and Cross Linker
Weight Percents Used in Mixing the Samples
(The epoxy to cross linker mole ratio was always kept at a 2:1 ratio.)

Sample Ratio	Wt % Epoxy	Wt % D-230	Wt % D-2000
2/1/0	77	23	0
32/15/1	69	20	11
22/10/1	66	18	16
18/8/1	63	18	19
12/5/1	59	15	26
6/2/1	55	13	32
9/3.5/1	48	10	42
4/1/1	40	6	54
9/1/3.5	35	4	61
6/1/2	32	2	66
12/1/5	31	2	67
18/1/8	29	1	70
2/0/1	27	0	73

The samples were placed in aluminum pans and crimped for use in the DSC to find their glass transition temperature. Each sample was scanned twice, starting at -50° C and gradually increasing to 150° C at 10° C/minute. This temperature range was chosen to ensure that the glass transition temperatures for all the materials would be found. The first run in the DSC is to remove any non-equilibrium effects that remain from the cure cycle. All the samples were analyzed, and those samples that exhibited a glass transition of 20° above room temperature or greater were chosen for further study in the DMA and Izod experiments. The reason for choosing these samples is that one can only perform

experiments on materials that exhibit the same distinct phase—in this case, the glassy phase. All the networks that had glass transition temperatures of 40° C and below exhibited rubber-like characteristics at room temperature and would not be suitable for structural applications.

The chosen systems were then cast into molds with the dimensions of 3.5 inches by 2.5 inches by 1.0 inch for further experiments. The preparation of the molds involved significantly more time and patience than with the pans. The total weight of each mold was around 160 grams, and with this much material, vigorous mixing for 15 minutes was required to ensure full reaction. The reaction was completed when the mixture changed from cloudy to clear. The dry mold was then coated with "Frekote," a silicone-releasing agent, and filled with the sample. The mold was placed into the vacuum oven for 2 hours operating at 15 inches mercury. Careful attention was made to ensure that the bubbles did not form too fast, which would result in an eruption of epoxy similar to that of a volcano. After 2 hours, a 25-inch mercury vacuum was pulled, again for 2 hours under careful supervision. Finally, a 29.5-inch mercury vacuum was pulled for 24 hours to ensure complete bubble removal. The reason for removing the bubbles is that even the smallest bubble will act as a crack initiation site resulting in premature failure and inaccurate results from the Izod experiment. The molds were then heated for 24 hours at 125° C to ensure complete cure. The curing time was obtained from the supplier of the epoxy and past studies with similar systems [16]. These epoxies were then removed from the molds and cut into 2.5-inch by 0.5-inch by 0.25-inch samples for future DMA and Izod experiments.

The samples for Izod experimentation were labeled according to their mole ratios and mailed to DESS[2] Machine, Smyrna, Delaware, to be precisely cut to match the requirements for the ASTM D-256 standard for Izod experimentation. This standard requires the samples to have a length of 2.5 inches, a width of 0.5 inch, and the thickness can vary among the samples as long as each sample has even thickness throughout. The width from the base of the notch to the other side must be 0.4 inch; this will ensure the correct notch radius. Once returned, the samples' length, width, and thickness were carefully measured with digital calipers to ensure that they matched the strict specifications of the ASTM standard. The dimensions of the machined samples are tabulated in Table 2.

The Izod experiment was performed at room temperature for all the samples. Six attempts were made on the 2/1/0 sample to obtain more accurate results, since the toughness of this sample will be used as a basis for comparison to the other four samples to see if the toughness increased. Three attempts at room temperature were performed on the other four samples, and the Izod reading was recorded. Since the glass transition temperatures of each of the five samples differ so much, three specimens from each of the five samples were placed into

---

[2]Not an acronym

liquid nitrogen for 7 to 8 minutes to ensure evaluation of each sample in glassy conditions. By doing this, one removes any biased results from the toughness, which are only increased by a difference in glass transition. This allows one to see if the bi-modal distribution really does increase the toughness. The final three specimens from each of the samples were used in the final Izod experiment. Each sample was cooled to 60° below its respective glass transition for 30 minutes; this again will ensure un-biased results. The cooling of the 32/15/1 samples was done with ice water which reached a temperature of 5° C. The cooling of the 22/10/1 samples was done with an ice water and alcohol solution to achieve 0° C. The final two samples required temperatures below 0° C; in order to do this, ethanol was cooled to its desired temperature with liquid nitrogen. The chilled solutions were placed into dewers to maintain a constant temperature. The 18/8/1 samples were cooled to -8° C, and the 12/5/1 samples chilled to -20° C.

Table 2. Sample Chart of Data Recorded for Each Specimen Before the Izod Experiment Was Performed

(The after-notch width indicates the width of the specimen from the base of the notch to the end of the sample. For this particular sample, two different types of Izod experiments were performed: one at room temperature and one with the specimens cooled with liquid nitrogen. Three Izod experiments were performed on the remaining four samples.)

Sample	Number	Length (in.)	Width (in.)	Thickness (in.)	After-Notch Width (in.)
2/1/0	2-1	2.502	0.502	0.236	0.408
	2-2	2.502	0.504	0.231	0.408
Room Temp	2-3	2.502	0.503	0.243	0.407
-----	2-4	2.504	0.503	0.227	0.408
-----	2-5	2.504	0.502	0.226	0.409
-----	2-6	2.503	0.502	0.229	0.410
Liquid	2-7	2.504	0.502	0.261	0.407
Nitrogen	2-8	2.504	0.502	0.216	0.405
-----	2-9	2.508	0.500	0.272	0.408
Liquid	2-10	2.505	0.501	0.253	0.404
Nitrogen	2-11	2.502	0.500	0.214	0.404
30 min.	2-12	2.504	0.502	0.225	0.407

The recorded data were corrected to account for windage and friction of the pendulum. This calculation was especially important because of the low impact strength of the samples. The correction factor was subtracted from the recorded

dial data, and this quantity was divided by the thickness of the sample. This final result is the impact strength of the material in foot-pounds per inch (ft-lb/in.).

Finally, the DMA experiments were performed on the five samples used in the Izod experiments. The results obtained from the DMA experiments will be storage modulus or stiffness of the material as a function of temperature. The purpose of these experiments is to determine whether the toughness of the material can be enhanced without loss of modulus or stiffness. The experiments were performed with a TA Instruments DMA with a film tension clamp. Each sample was machined to the specifications required by the experiment by a slow speed saw. Table 3 gives the length, width, and thickness of the five samples used.

Table 3. Dimensions of the Five Samples Used in the DMA
Experiments as Required by the Manufacturer

Sample	Length (in.)	Width (in.)	Thickness (in.)
2/1/0	24.68	4.74	0.96
32/15/1	21.74	4.77	1.29
22.10/1	22.74	4.77	1.04
18/8/1	21.06	4.73	0.91
12/5/1	20.95	4.83	1.04

After cutting, each sample was placed in the clamping device lengthwise and the screws were hand tightened on both top and bottom. Then the screws were given a quarter turn with a torque wrench that applied 1 to 2 ft-lb of torque. Even though this amount of torque was less than recommended, any more resulted in the compression of the specimen and ultimate failure during the experiment. The DMA cooled each sample to 75° C below its respective glass transition temperature via liquid nitrogen. This will ensure an even baseline before any transition will begin. Then each sample was gradually increased to 120° C at 5° C per minute with 0.01 Newton as an initial static force with a 1-Hz oscillation of 1.5 Newtons. Finally, the storage modulus at various temperatures could be read from the graph and compared to the impact strength for each specific sample.

14

6. Results

The results show that as the cross-link density decreases, the glass transition temperature decreases, as expected. The Br-DGEBA system, which was first used to conduct the research, has been abandoned, even though the glass transition temperatures have been found. The abandonment was because of the extreme difficulty of removing the bubbles from the molds with a vacuum oven. The reason the bubbles did not want to come out is because the Br-DGEBA system is a solid at room temperature. Any attempts to increase the temperature to the system's melting point and still pull a 29.5-inch mercury vacuum resulted in a bubbly mess of epoxy because the bubbles were being removed too fast. Therefore, a smaller vacuum was pulled while remaining at the melting point of the system. The only problem with this approach is that when the temperature was increased, the cure cycle started and the epoxy cured before all the bubbles could get out. This bubble removal problem led to the conclusion that this system could not be used to conduct further research.

These results showed that an epoxy system, which was liquid at room temperature, must be chosen if bubble removal was to take place. This led to the choice of the EPON 828 epoxy system, which is very similar to the Br-DGEBA system, except that the EPON system is not brominated. The same experiments were run with the EPON system to find the glass transition temperature of each of the mole ratios. The results were just as expected: the lower the cross-link density, the lower the glass transition. Figures 7 and 8 show two graphs (one for the Br-DGEBA system and one for the EPON 828 system) which demonstrate how the increase of the mole percent of D-2000 (and thus the decrease in cross-link density) affects the glass transition. The sample number, weight-percent D-230, and corresponding glass transition temperatures are compiled in Table 4.

These two graphs show that the cross-link density has a direct impact on the glass transition temperature and therefore on the toughness of the material. Notice how much the glass transition temperature in Figure 2 falls with just the slight addition of D-2000. Also, the glass transition temperature of the EPON 828 system is affected much more by the addition of D-2000 because of the low molecular weight of the EPON epoxy. The results of Figure 8 show that a 5:1 ratio of D-230 to D-2000 is the lowest system that can be used in further experiments because its T_g glass transition is the last system to be 20° or more above room temperature.
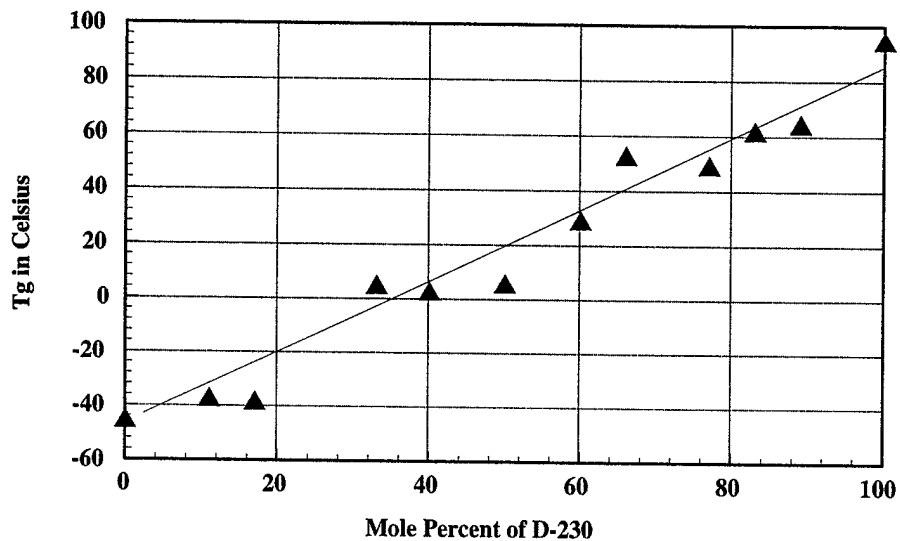
Figure 7. Glass Transition Versus the Percent D-230 in a Br-DGEBA Epoxy System. (Notice how much the temperature drops with just a small percent of D-2000. As the mole percent of D-230 decreases, the mole percent of D-2000 increases, so at 80 mole % D-230, there is 20 mole % D-2000 present.)
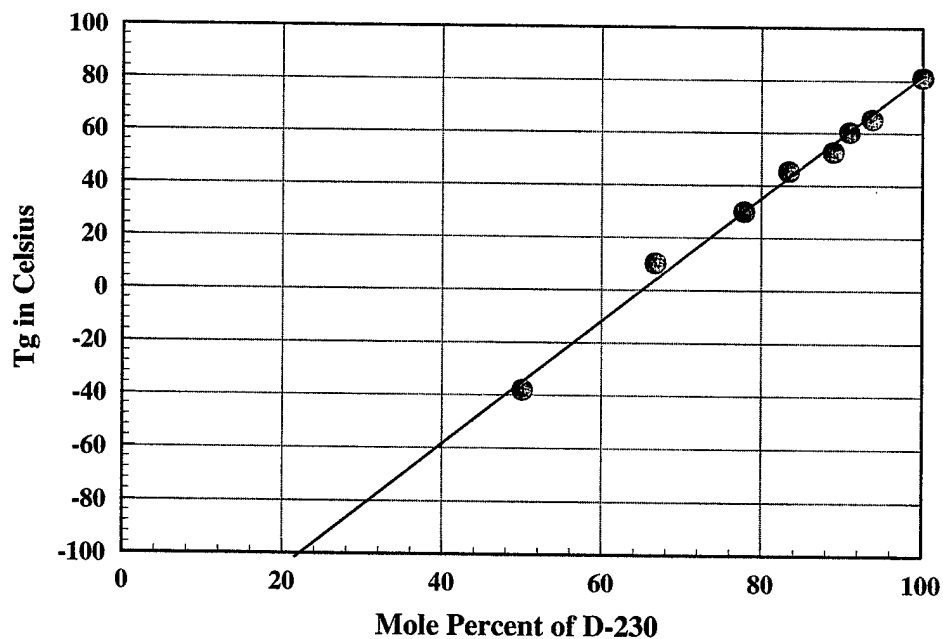

Figure 8. Glass Transition Versus Mole Percent D-230 With an EPON 828 Epoxy System.

16

Table 4. Reference Table for Figures 7 Through 22

Sample	Wt % Epoxy	Wt % D-230	Wt % D-2000	T_g (C)
2/1/0	77	23	0	80
32/15/1	69	20	11	65
22/10/1	66	18	16	60
18/8/1	63	18	19	57
12/5/1	59	15	26	43

7. Discussion

Each of the following figures shows how the toughness is correlated with the mole percent of D-230, the glass transition temperature, or the storage modulus. Figure 9 shows the relationship between the impact strength and the mole percent of D-230 at room temperature. Here, the results are to be expected; the impact strength increases with a decrease in mole percent D-230, showing that there is a direct relationship between the resin composition and the impact strength. Figure 10 shows the same relationship, but this time at –180 °C, with liquid nitrogen. Here, each sample is evaluated well below its glass transition, so now a true comparison can be made between the samples. The results for the 2/1/0 and the 32/15/1 samples seem to be a little high, suggesting that the impact strength may stabilize at high D-230 content.

Figure 11 shows the same relationship again for impact strength measured at 60° C below each sample's respective glass transition temperature. These temperature conditions will normalize the experiment so that unbiased results can be obtained which compare the impact strength and the cross-link density. The results here differ greatly from those in the previous two studies. The impact strengths for the 2/1/0 and 32/15/1 samples stayed the same from the room temperature results, while the other three did not. Again, this should be the case since their respective glass transition temperatures are already well above room temperature, and cooling them any further should have no effect on the toughness. The other three samples' glass transition temperatures are in the region of instability, ±20° C of the reported glass transition temperature, at room temperature.
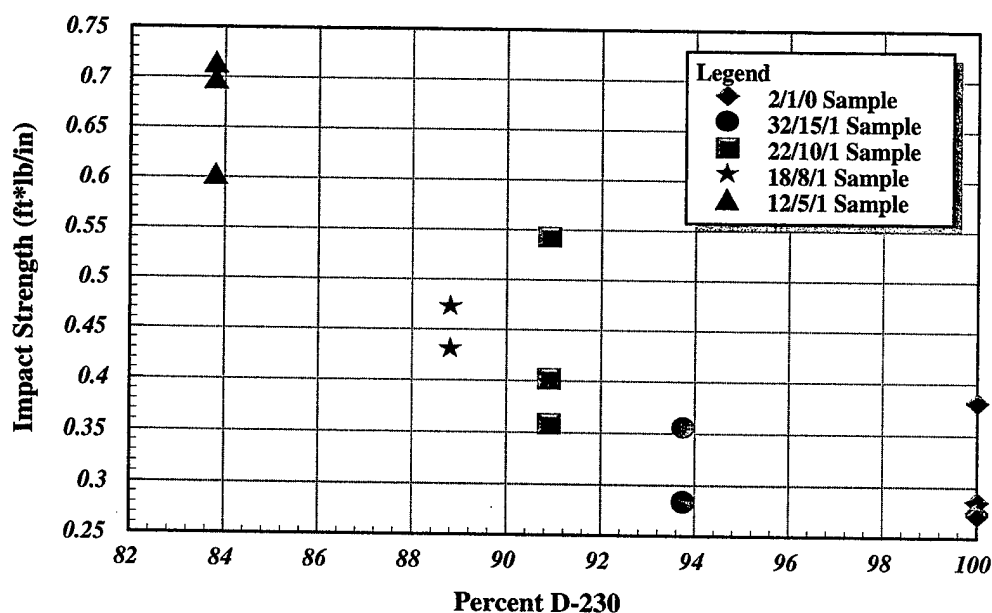
Figure 9. Impact Strength Versus Mole Percent D-230 at Room Temperature. (Notice how the impact strength increases as the mole percent decreases. This directly shows that the impact strength increases with decreasing cross-link density.)
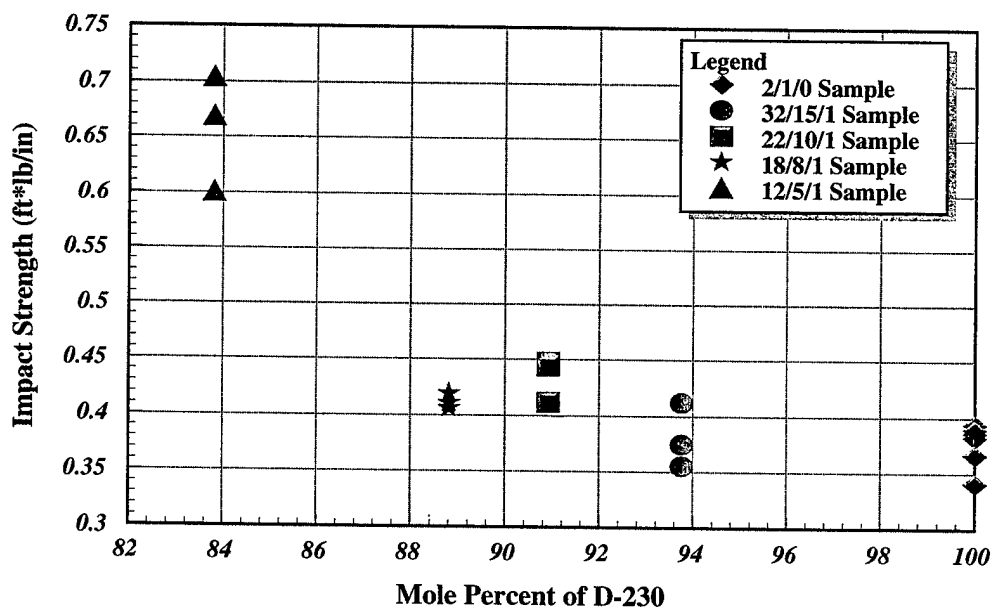

Figure 10. Impact Strength Versus Mole Percent D-230 at -180° C. (Notice the decrease in impact strength from those at room temperature, except for the 12/5/1 sample, which did not change.)
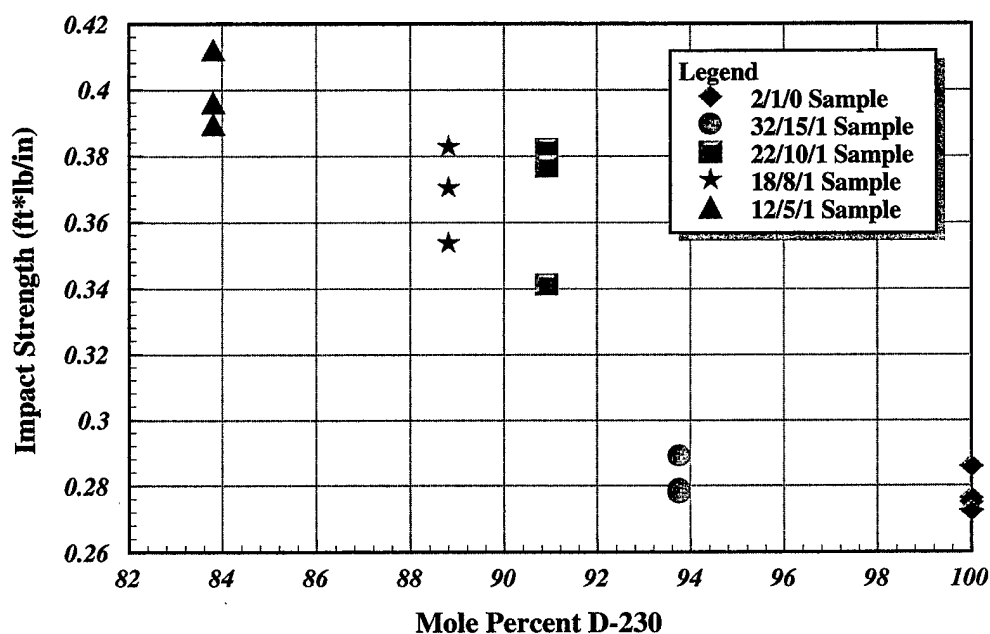
18

Figure 11. Impact Strength Versus Mole Percent D-230 at T_g–60° C. (Here, the results are similar to those taken at 180° C except now the 12/5/1 sample falls on a linear line with the rest.)

The instability refers to when the sample is not completely in the glassy state or the rubbery state but more like a hybrid state. We would therefore expect their impact strengths to fall when measured at 60° C below their respective glass transition temperature (T_g-60 °C) because the room temperature experiment was done in that region of instability where the epoxies contained some rubber-like character. The 22/10/1 and the 18/8/1 samples' impact strengths fell only about 0.05 ft-lb/in, which is to be expected since we are far away from their glass transition temperatures. The 12/5/1 sample fell about 0.30 ft-lb/in, which is a large drop compared to the others. This shows us that the true impact strength for the 12/5/1 sample is not really that high when compared to the others. These results were to be expected because at a lower temperature, a material becomes brittle and its toughness decreases. Now we can compare each sample and draw a conclusion that at a normalized temperature, there is only a small improvement in the toughness of the epoxy from the bi-modal network. When comparing these results to those in Figure 10, we would expect the results to be similar because both studies are done at a temperature well below the glass transition temperatures, but this is not the case. We can only conclude that the experiments done at the liquid nitrogen temperature may have been tainted. The linear relationship between impact strength and cross-link density was maintained for all the experiments.

19

Figures 12 through 14 are the average results for the three impact strength measurements conducted for each sample at the three different temperatures chosen, with error. Notice that the error is very small for some of the results but large for others, and this is consistent for each experiment. Notice that the T_g-60° C experiments have the greatest error overall among all five different D-230 ratio samples. Thus, one should use caution to include the error range when comparing exact values of the impact strength measured during different conditions. Figure 15 compares the results of each experiment. One can see that the liquid nitrogen results are similar to the room temperature results, within experimental error, and that the liquid nitrogen values are higher than the T_g-60° C values. This also suggests that the liquid nitrogen values are unusually high and may be tainted.
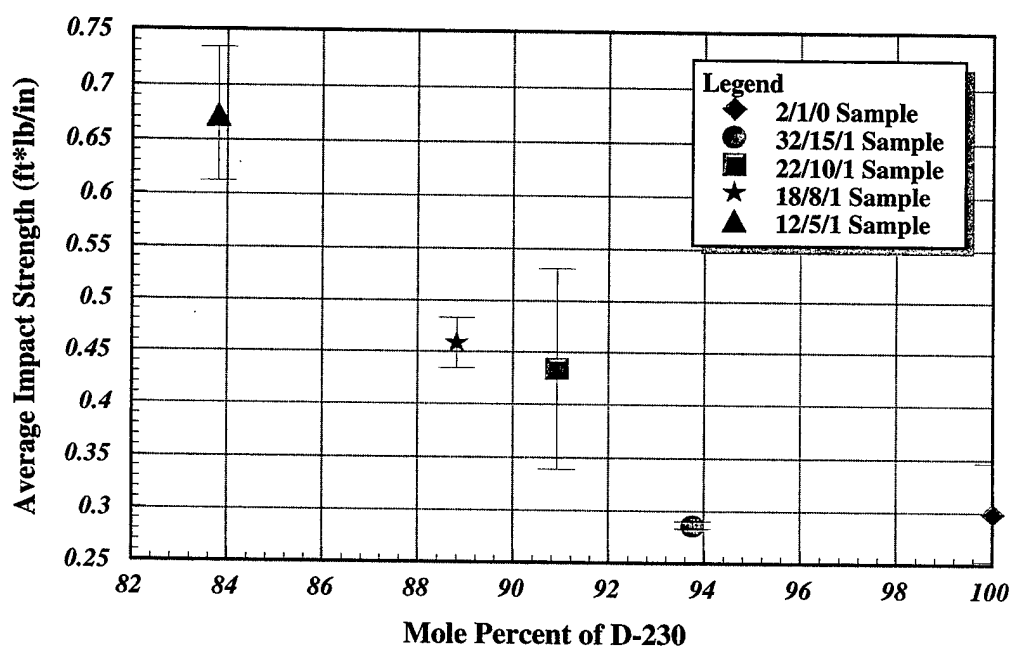

Figure 12. Average Impact Strength Versus Mole Percent D-230 at Room Temperature. (Here are the combined results from the room temperature experiments with error. Notice how the 32/15/1 sample is lower than the 2/1/0 sample, contrary to expectations.)
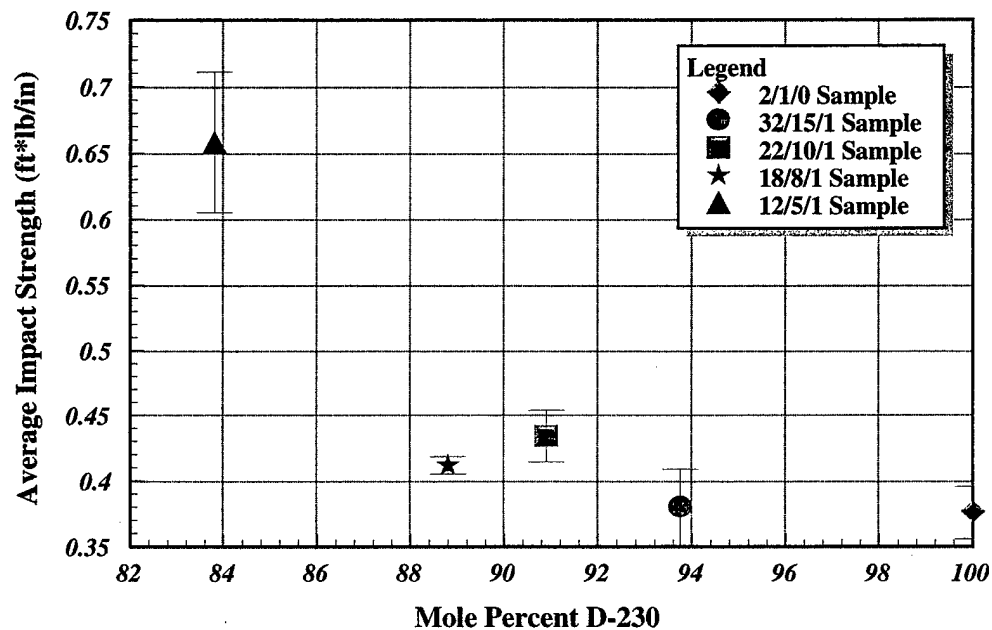
Figure 13. Average Impact Strength Versus Mole Percent D-230 at -180° C. (Here are the combined liquid nitrogen results with error. Again notice the 32/15/1 ratio is lower than the 2/1/0.)

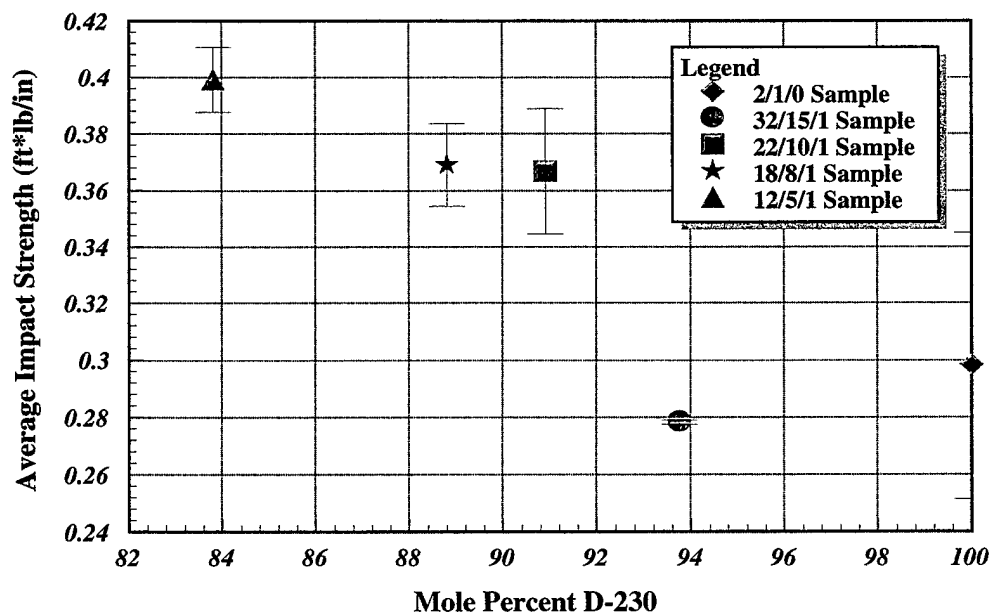Figure 14. Average Impact Strength Versus Mole Percent D-230 at T_g-60° C. (Here are the compiled results with error. Again the 32/15/1 sample is lower than the 2/1/0.)
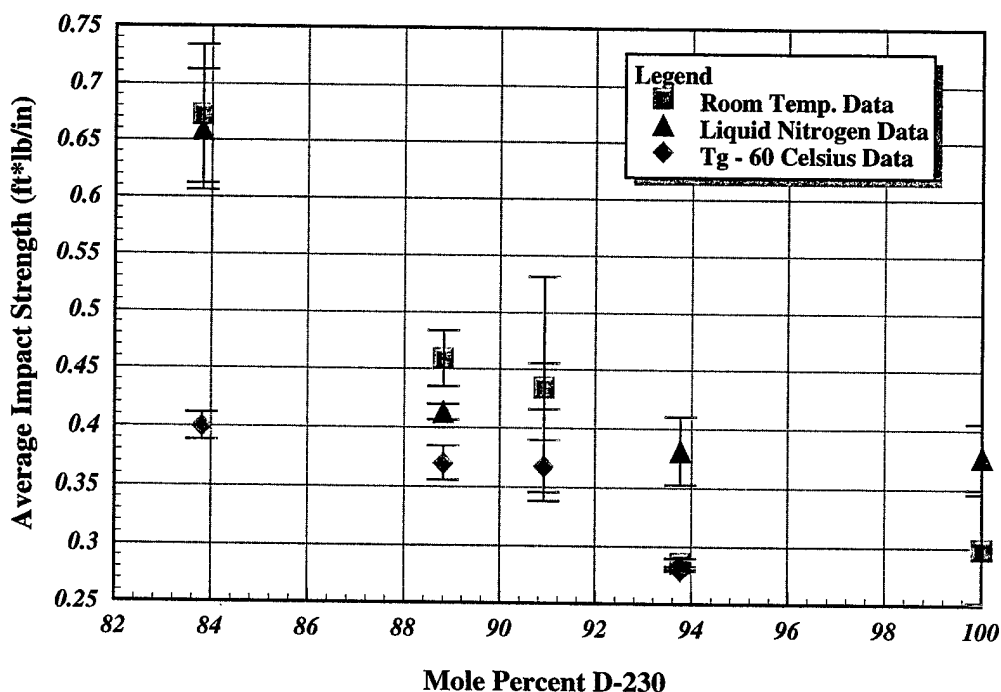
21

Figure 15. Average Impact Strength Versus Mole Percent D-230 With Error.

The next three graphs, Figures 16 through 19, show the impact strength versus the glass transition temperature. These results show the same trend when compared to Figures 12 through 14, which should be the case since the mole percent of D-230 is directly related to the glass transition temperature. Here, you can also see that the impact strength increases with a decrease in the glass transition temperature, again proving that there is an inverse relationship between impact strength and cross-link density. Figures 19 through 23 show the average impact strength versus experimental temperature for each of the five samples. Here, one can see the different results obtained with each of the three experiments. The 2/1/0, 32/15/1, and 22/10/1 samples show very little difference in the impact strength among the three results, while the 18/8/1 and the 12/5/1 samples' impact strengths vary considerably among the three experiments. The results for the 18/8/1 and the 12/5/1 samples in Figures 22 and 23 were expected. Their glass transition temperatures are very close to room temperature, so their toughness is very dependent on the experimental temperature. The other three samples displayed the logical result since their glass transition temperatures are farther from room temperature.
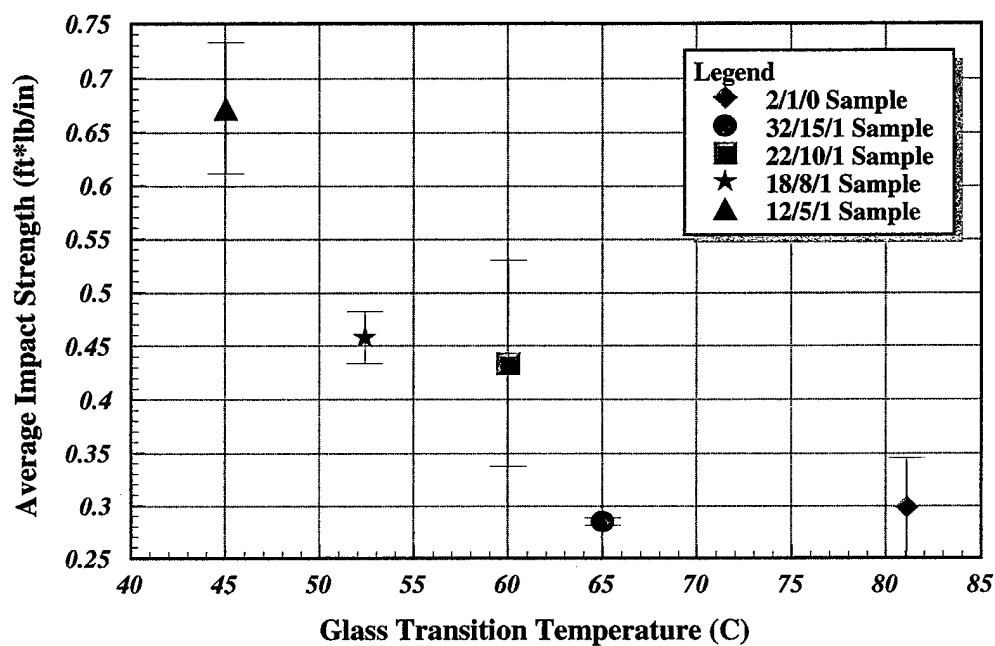
22

Figure 16. Average Impact Strength Versus Glass Transition Temperature at Room Temperature With Error. (Notice how it follows the same trend as Figures 8 through 13.)
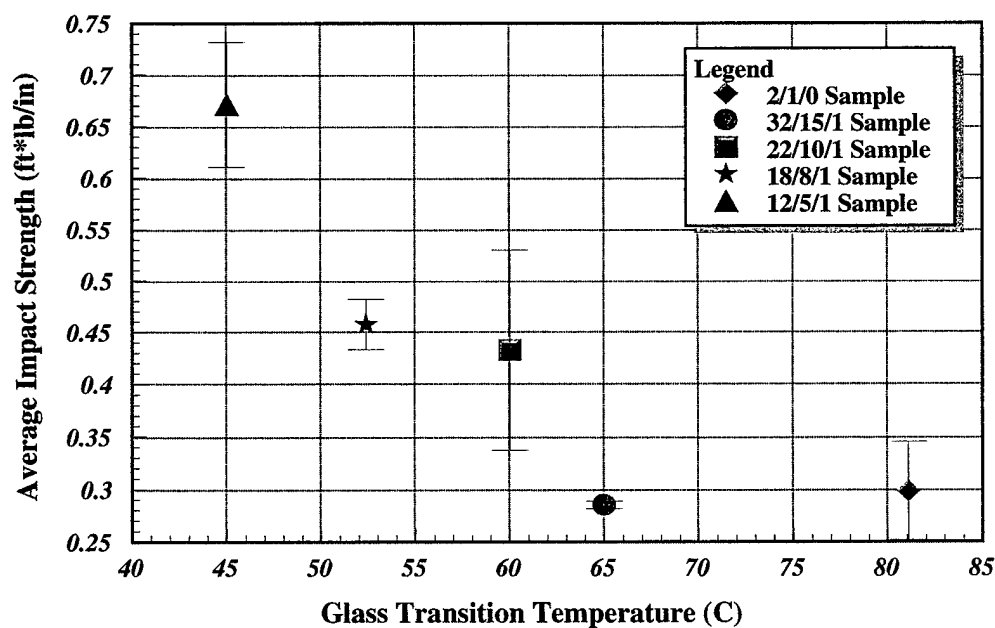

Figure 17. Average Impact Strength Versus Glass Transition Temperature at –180° C, With Error. (Again it follows the same trend as Figures 8 through 13.)
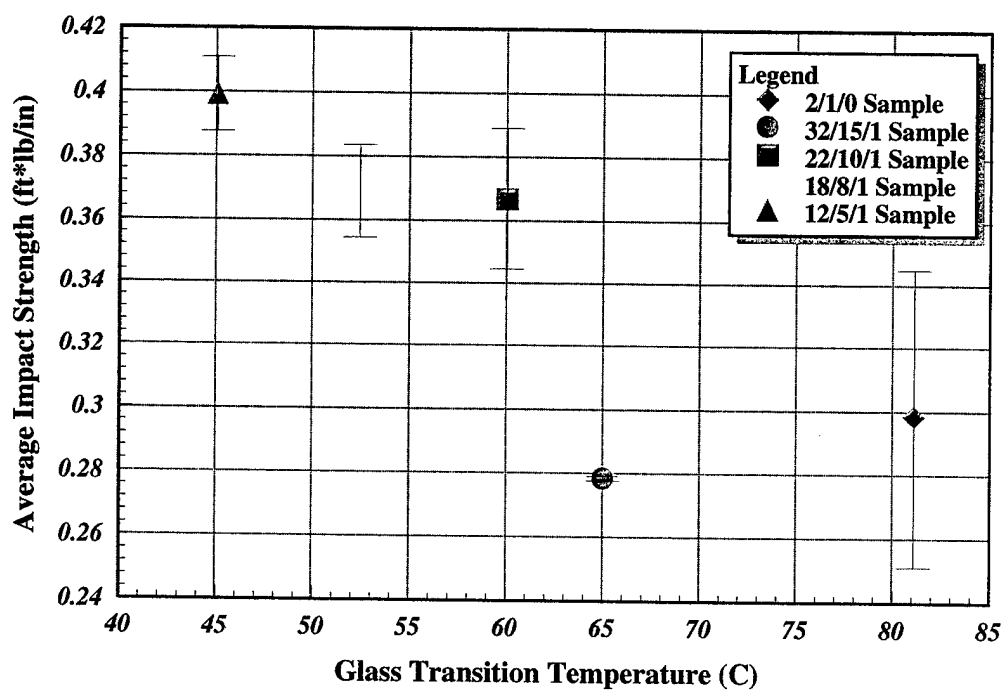
Figure 18. Average Impact Strength Versus Glass Transition Temperature at 60°C Below T_g With Error. (Again it follows the same trend as Figures 9 through 14.)
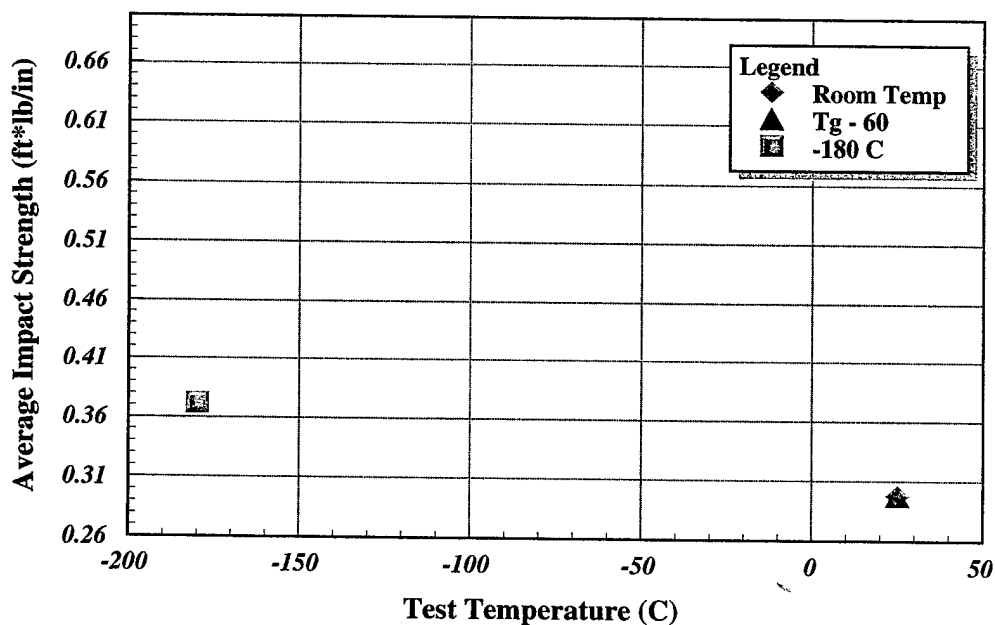

Figure 19. Average Impact Strength Versus Experimental Temperature for 100 mole % D-230. (Notice how the room temperature results and the T_g-60° C are very similar, which is not as expected. Also the impact strength at –180° C was expected to be lower than those at room temperature.)
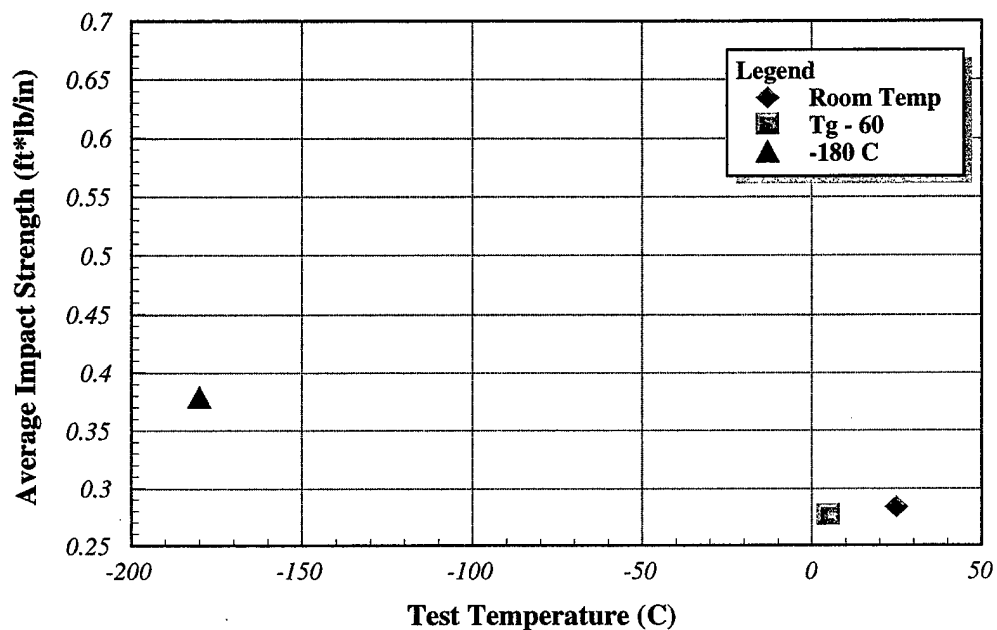
Figure 20. Average Impact Strength Versus Experimental Temperature for 93 mole % D-230. (This graph displays the same characteristics as Figure 19.)

Figure 21. Average Impact Strength Versus Experimental Temperature for 90 mole % D-230. (These results are consistent with the expected results that the impact strength at –180° C should be less than those at room temperature.)
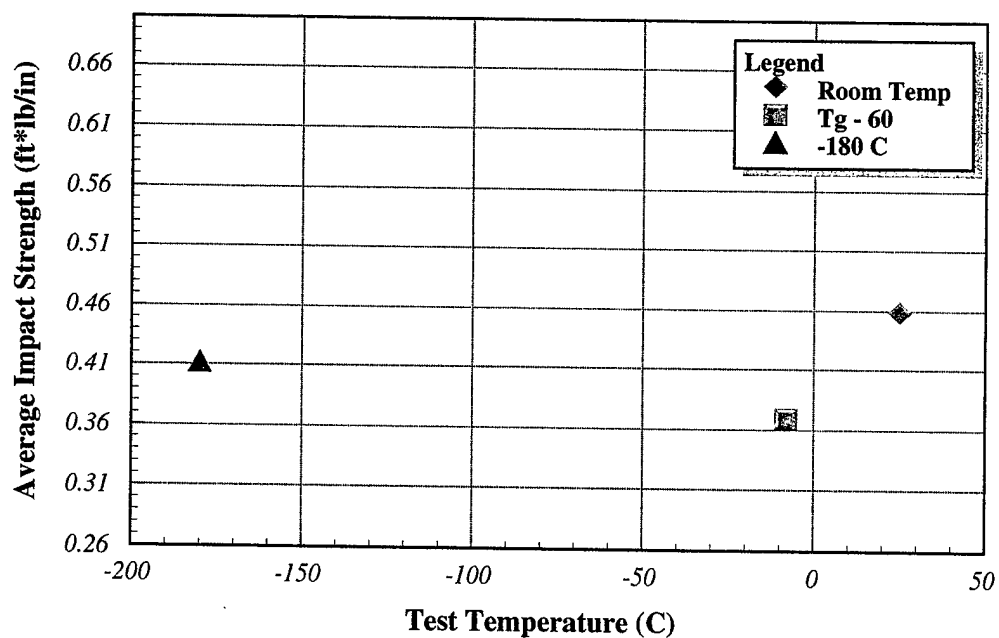
Figure 22. Average Impact Strength Versus Experimental Temperature for 88 mole % D-230. (This figure follows the same trend as Figure 21.)

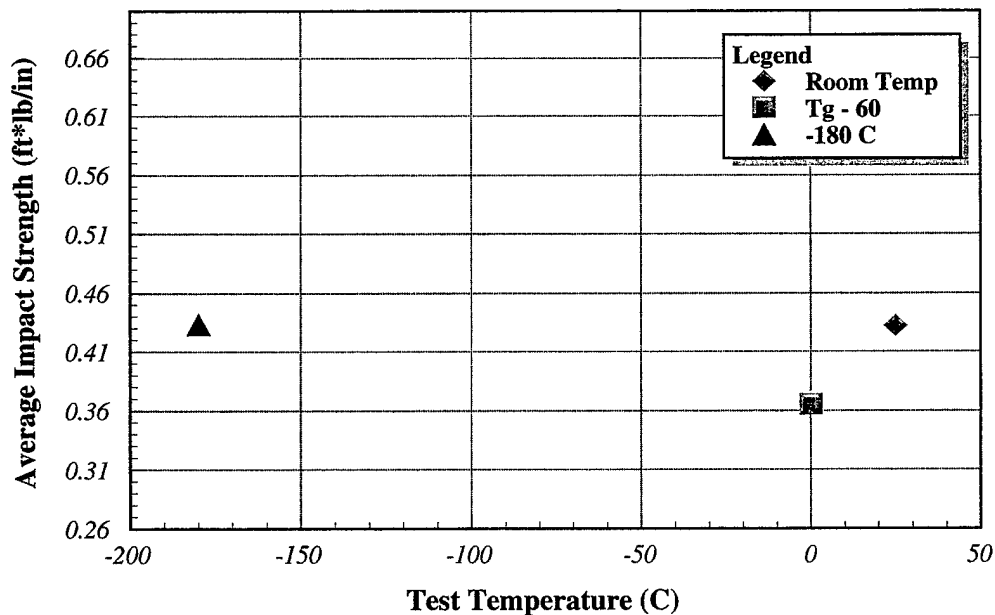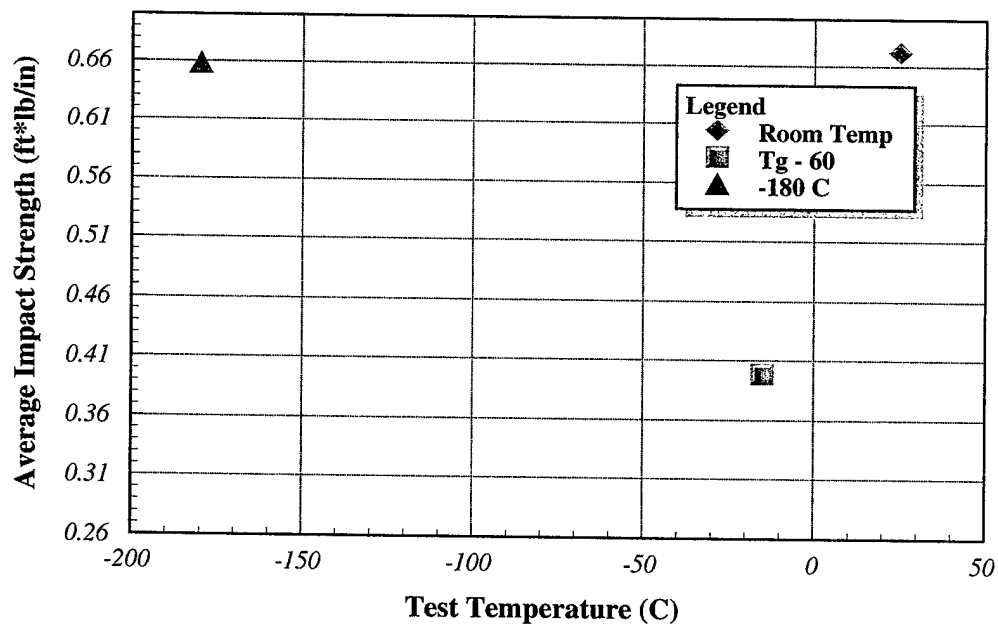Figure 23. Average Impact Strength Versus Experimental Temperature for 84 mole % D-230. (Notice how this figure follows the same trend as in Figures 21 and 22, but there is more scatter present in the results.)

26
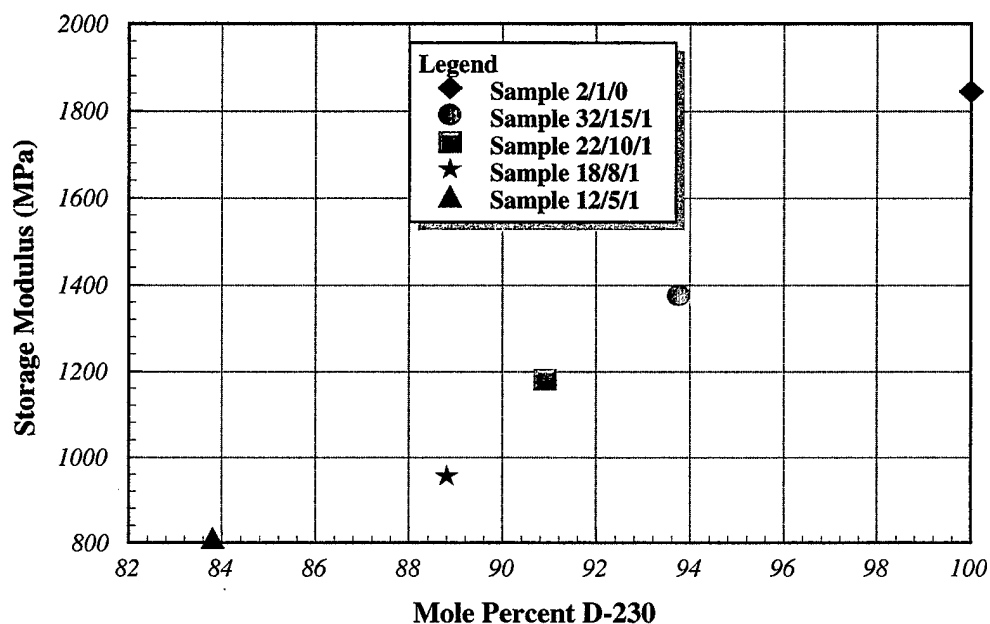
Figure 24. Storage Modulus Versus Mole Percent D-230 at Room Temperature. (Notice the linear trend that is very similar to the DSC results, Figure 8.)
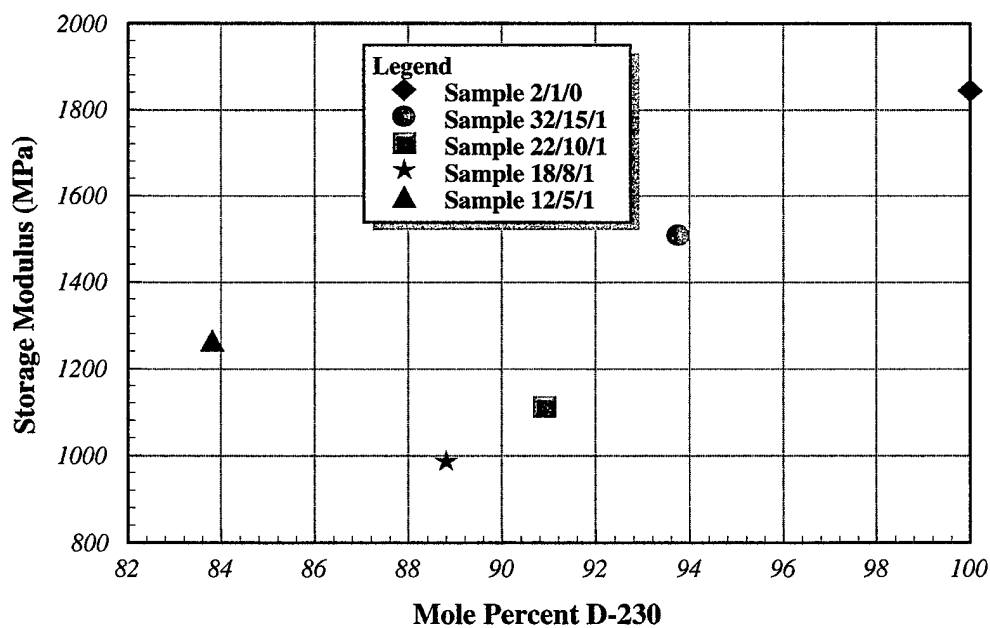
Figure 25. Storage Modulus Versus Mole Percent D-230 at T_g– 60° C. (Notice the linear relationship that is similar to Figure 24, except for sample 12/5/1 whose modulus actually increased with a decrease in temperature.)

Next, the storage modulus versus mole percent D-230 relationship is shown at room temperature and at T_g-60° C. The results primarily follow a linear relationship between the storage modulus and the mole percent D-230, but we can see that the 12/5/1 sample does not follow this pattern. Here, the storage modulus at T_g-60° C is increased by 500 MPa beyond its room temperature value, which should be the case since a decrease in temperature stiffens the material and increases the modulus. However, this increase is about 5 times greater than the increase in the 32/15/1 and 18/8/1 samples and shows that something is definitely different with the 12/5/1 sample. One may conclude that far away from the glass transition temperature and with a low cross-link density, the bi-modal nature of the network is having some effect. Figure 26 shows the effect of the glass transition on the storage modulus; the relationship is linear as to be expected from previous discussions. Figure 27 shows how the storage modulus is related to impact strength at room temperature. Here, one can see that when the impact strength increases, the storage modulus decreases. This is the usual result but is not what we wanted to happen; we hoped to increase toughness without a loss in modulus. Here, we can see that the bi-modal network does decrease the modulus of the epoxy, which may be undesirable. When this study is done at -60° C from the glass transition, the 12/5/1 sample with the highest impact strength actually has a larger storage modulus than the 18/8/1 and 22/10/1 samples, which have lower impact strengths. Even though Figure 28 displays the results we wanted for the 12/5/1 sample, an increase in strength without a great loss in modulus, the results were obtained at –18° C. Thus, the results may be of limited use since most design is for applications at room temperature.
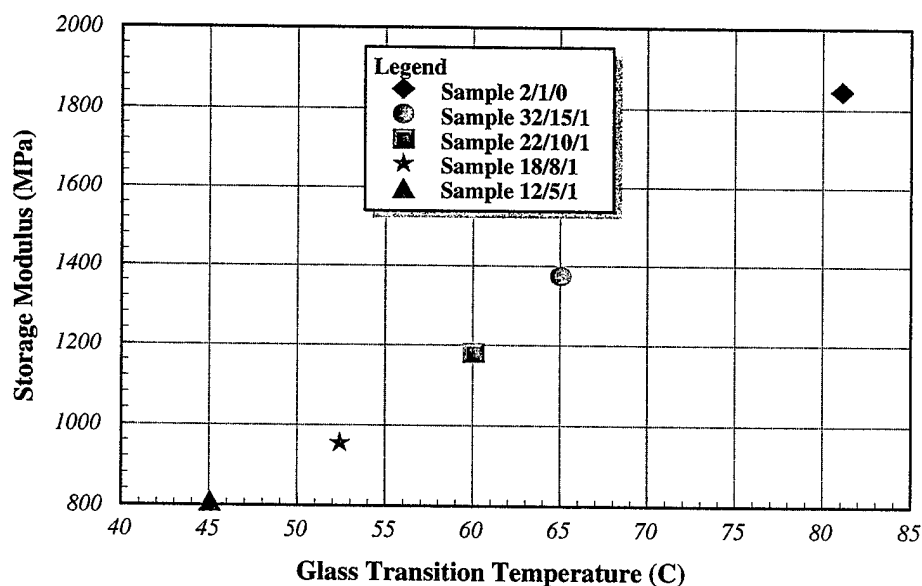
Figure 26. Storage Modulus Versus Glass Transition Temperature. (Again this graph displays the same trend as Figure 24, which is to be expected since there is a direct relationship between cross-ink density and glass transition.)

28
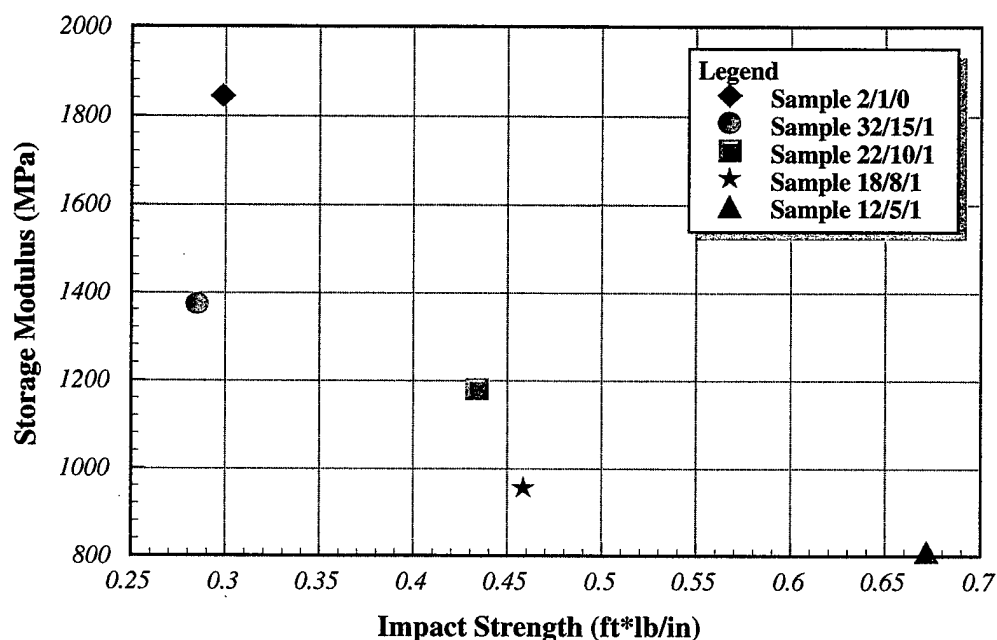
Figure 27. Storage Modulus Versus Impact Strength at Room Temperature. (This figure shows that there is a loss in modulus as the impact strength increases.)
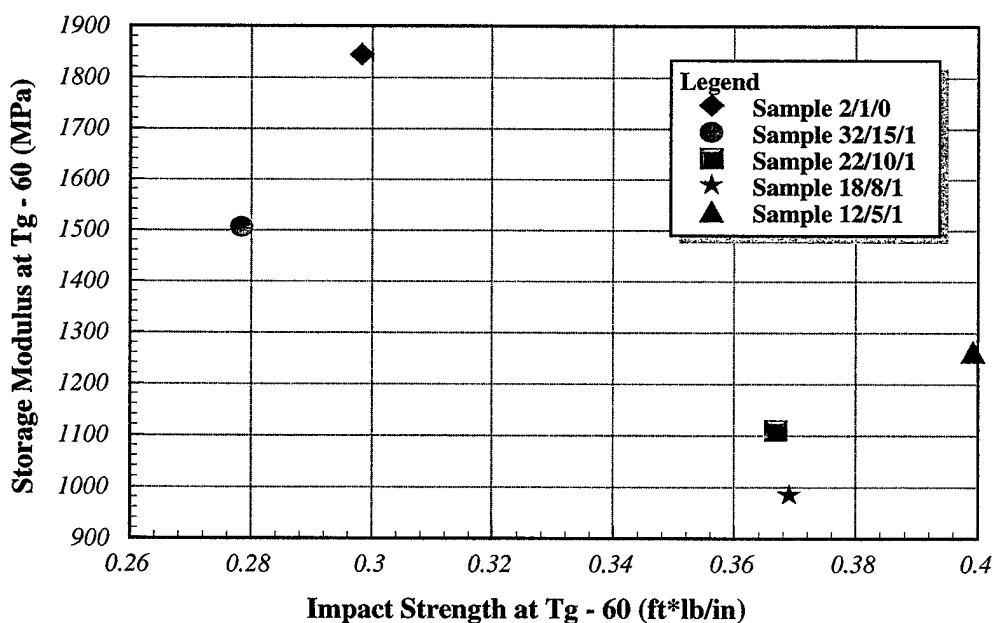
Figure 28. Storage Modulus Versus Impact Strength at $T_g - 60°$ C. (Notice the scatter in this figure. The storage modulus should decrease with increasing impact strength; apparently this is not the case for the 12/5/1 sample.)

8. Conclusion

A study of the relationship between a bi-modal cross-link distribution in an epoxy matrix and the mechanical properties of the material has been completed. We can conclude that there is a linear relationship between the cross-link density and the glass transition temperature, not only for the EPON 828 system but also for the Br-DGEBA system. This shows us that this relationship should hold for all epoxy systems with varying cross-link densities. From this relationship, one can choose a set of samples to study, all of which have glass transition temperatures of 20°C or more above room temperature.

From the Izod and DMA studies of the five chosen systems, we can draw several conclusions. The cross-link density has a direct relationship with the impact strength; as the cross-link density decreases, the impact strength increases. We can also conclude that the toughness of the material is increased with a decrease in cross-link density. The studies performed at 60°C below the glass transition temperature were found to give true, normalized results. These results showed us that the bi-modal distribution did not increase toughness as much as the room temperature results suggested for the 12/5/1 sample. When the study was performed at −180°C, the results were very different from what could reasonably be expected and no logical conclusion could be made from them.

The DMA results proved to be the most revealing in this study. Here, we could see that the bi-modal distribution did increase the impact strength but not without a loss in modulus. This is what usually occurs but not what we wanted to happen. A new material that has increased toughness but loss of stiffness has little value over what is currently available. Even though the results obtained at 60°C below the glass transition temperatures showed some promise in giving us strength plus toughness in EPON 828/Jeffamine systems, these results are not very useful because most applications do not require materials designed for use in a −18°C environment. However, it is possible that with a different choice of cross linkers and epoxies, a bi-modal cross-link distribution may offer some improved properties. Finally, one can conclude that the bi-modal distribution did increase the toughness of the material but with a loss in modulus.

References

1. Encyclopedia of Polymer Science, Vol. 6, pp. 322-330, Wiley & Sons, New York, 1985.

2. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 9, pp. 730-750, Wiley & Sons, New York, 1985.

3. Shackelford, J.F., "Introduction to Materials Science for Engineers," p. 640, Prentice Hall, New Jersey, 1996.

4. Dieter, G.E., "Mechanical Metallurgy," pp. 275, 492, 494, and 495, McGraw-Hill Co., New York, 1976.

5. Ward, I.M., "Mechanical Properties of Solid Polymers," pp. 88 and 178, Wiley and Sons, New York, 1993.

6. Beck-Tan, N.C., "Structure in Bimodal Epoxy Networks: A small Angle Scattering Study," Lecture at U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, 1997.

7. Madkour, T.M, and M.S. Handi, "Elastomers with Two Cross-linking Systems of Different Lengths Viewed as Bimodal Networks," Journal of Applied Polymer Science, Vol. 61, pp. 1239-1244, 1996.

8. Cukierman, S., J-L. Halary, and L. Monnerie, "Dynamic Mechanical Response of Model Epoxy Networks in the Glassy State," Polymer Engineering and Science, , Vol. 31, No. 20, October 1991.

9. Espuche-Urbaczewski, E., J. Galy, J-F. Gerand, J-P. Pascoult, and H. Sautereau, "Influence of Chain Flexibility and Cross-link Density on Mechanical Properties of Epoxy/Amine Networks," Polymer Engineering and Science, Vol. 21, No. 22, pp. 1572-1580, November 1991.

10. Sharaf, M.A., and J.E. Mark, "Elastomers Having High Functionality Cross Links Viewed as Bimodal Networks. An Alternative Interpretation in Terms of Bimodal Chai-Length Distributions," Journal of Polymer Science: Part B: Polymer Physics, Vol. 33, pp. 1151-1165, 1995.

11. Hwang, J.-F., J.A. Manson, R.H. Hertzberg, G.A. Miller, and L.H. Sperling, "Structure-Property Relationships in Rubber-Toughened Epoxies," Polymer Engineering and Science, Vol. 29, No. 20, pp. 1466-1476, October 1989.

12. Vallo, C.I., "Toughened-hybrid Epoxies: Influence of the Rubber-Phase Morphology on Mechanical Properties," Journal of Materials Science, Vol. 29, pp. 2481-2486, 1994.

13. Mulkern, T.J., Personal Conversation at the U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, 1997.

14. Wunderlich, B., "Thermal Analysis," pp. 30, 71, 222, 244, 352, and 355, Academic Press, Inc., San Diego, CA., 1990.

15. Cox, C.T., M.R. Ottaway, and R.E. Wetton, "Dynamic Mechanical Thermal Analyzer; A New Instrument and its Applications to Polymeric Materials," taken from Proceedings of the Second European Symposium on Thermal Analysis, edited by Dollimore, David, Heyden, and Son Ltd., London, 1981.

16. Wu, Wen-Li, and B.J. Bauer, "Epoxy Network Structures 3. Neutron — Scattering Study of Epoxies Containing Monomers of Different Molecular Weights," Macromolecules, Vol. 19, No. 6, p. 1613, 1986.

APPENDIX A

SAMPLE CALCULATIONS

INTENTIONALLY LEFT BLANK

SAMPLE CALCULATIONS

Sample Calculations: Wind Correction Factor for Izod Tests

$h_m := 2 \cdot ft$

$L := \left(\dfrac{g}{4 \cdot \pi^2}\right) \cdot (1.36 s)^2$

$E_a := 0.03 \cdot ft \cdot lb$

$E_m := 2 \cdot ft \cdot lb$

Maximum height of center of gravity of pendulum at start of test

Distance from fulcrum to center of gravity of pendulum

Energy correction for windage and friction.

Full scale reading from pendulum used

$E_s := 0.09 \cdot ft \cdot lb$

Taken from the Izod reading of sample 2 - 4.

$$B_{max} := acos\left[1 - \left[\left(\dfrac{h_m}{L}\right) \cdot \left(1 - \dfrac{E_a}{E_m}\right)\right]\right]$$

Maximum angle pendulum will travel with one swing of the pendulum.

$$B := acos\left[1 - \left[\left(\dfrac{h_m}{L}\right) \cdot \left(1 - \dfrac{E_s}{E_m}\right)\right]\right]$$

Angle traveled for a given specimen

$E_b := 0.01 \cdot ft \cdot lb$

Second correction for windage

$t := 0.227 in$
Thickness of sample 2 - 4.

$$E_{tc} := \left[E_a - \left(\dfrac{E_b}{2}\right)\right] \cdot \left(\dfrac{B}{B_{max}}\right) + \left(\dfrac{E_b}{2}\right)$$

Total energy correction for the breaking energy of a specimen.

$$I_s := \dfrac{\left(E_s - E_{tc}\right)}{t}$$

$$I_s = \bullet \dfrac{ft \cdot lb}{in}$$

Sample Calcualtions

Here is a sample calcualtion for the weight fractions of epoxy and cross linkers.

$$MW_{epoxy} := 377$$

$$MW_{D230} := 230$$

$$MW_{D2000} := 2000$$

$$Moles_{epoxy} := \begin{bmatrix} 2 \\ 32 \\ 22 \\ 18 \\ 12 \\ 6 \\ 9 \\ 4 \\ 6 \\ 9 \\ 12 \\ 18 \\ 2 \end{bmatrix} \quad Moles_{D230} := \begin{bmatrix} 1 \\ 15 \\ 10 \\ 8 \\ 5 \\ 2 \\ 3.5 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 0 \end{bmatrix} \quad Moles_{D2000} := \begin{bmatrix} 0 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 2 \\ 3.5 \\ 5 \\ 8 \\ 1 \end{bmatrix}$$

$$Total_0 := MW_{epoxy} \cdot Moles_{epoxy_0} + MW_{D230} \cdot Moles_{D230_0} + MW_{D2000} \cdot Moles_{D2000_0}$$

$$Total_0 =$$

$$Wt_{\%.epoxy} := \frac{MW_{epoxy} \cdot Moles_{epoxy_0}}{Total_0} \cdot 100 \qquad Wt_{\%.epoxy} =$$

$$Wt_{\%D230} := \frac{MW_{D230} \cdot Moles_{D230_0}}{Total_0} \cdot 100 \qquad Wt_{\%D230} =$$

$$Wt_{\%D2000} := \frac{MW_{D2000} \cdot Moles_{D2000_0}}{Total_0} \cdot 100 \qquad Wt_{\%D2000} =$$

Sample Calculations: Error Analysis for the Izod Imapct Testing

In this method we will use the standard **t-test** for finding the 80% confidence interval. The 80% confidence interval is commonly used for engineering materials.

Part a. Room Temperature Study   80 % confidence $t := 1.476$

The Impact data for the 2/1/0 sample

$Avg := 0.298277599$ $StD := 0.0467935$ $n := 5$

$Error := t \cdot \dfrac{StD}{\sqrt{n}}$ $Error = 0.031$

Impact data for the rest of the samples $n := 2$ $t := 1.886$

$$Avg := \begin{bmatrix} 0.285099444 \\ 0.433714104 \\ 0.458319971 \\ 0.671694963 \end{bmatrix} \qquad StD := \begin{bmatrix} 0.0035134 \\ 0.096455 \\ 0.024203 \\ 0.060573 \end{bmatrix}$$

$$Error := t \cdot \dfrac{StD}{\sqrt{n}} \qquad Error = \begin{bmatrix} 4.685 \cdot 10^{-3} \\ 0.129 \\ 0.032 \\ 0.081 \end{bmatrix}$$

Part b: -180 °C Study

All samples

$$Avg := \begin{bmatrix} 0.376528044 \\ 0.380550491 \\ 0.434780393 \\ 0.412384705 \\ 0.657987539 \end{bmatrix} \qquad StD := \begin{bmatrix} 0.019867714 \\ 0.02887 \\ 0.019798 \\ 0.0065898 \\ 0.05288 \end{bmatrix} \qquad Error := t \cdot \dfrac{StD}{\sqrt{n}} \qquad Error = \begin{bmatrix} 0.026 \\ 0.039 \\ 0.026 \\ 8.788 \cdot 10^{-3} \\ 0.071 \end{bmatrix}$$

37

Part c: Tg - 60 Study

All the samples except the 2/1/0 because the results are the same as in part a

$$\text{Avg} := \begin{bmatrix} 0.278408289 \\ 0.366779015 \\ 0.369025341 \\ 0.399192698 \end{bmatrix} \qquad \text{StD} := \begin{bmatrix} 0.000755717 \\ 0.022154961 \\ 0.014534063 \\ 0.011574018 \end{bmatrix} \qquad \text{Error} := t \cdot \frac{\text{StD}}{\sqrt{n}} \qquad \text{Error} = \begin{bmatrix} 1.008 \cdot 10^{-3} \\ 0.03 \\ 0.019 \\ 0.015 \end{bmatrix}$$

NO. OF
COPIES ORGANIZATION

1	ADMINISTRATOR DEFENSE TECHNICAL INFO CTR ATTN DTIC OCA 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218
1	DIRECTOR US ARMY RSCH LABORATORY ATTN AMSRL CI AI R REC MGMT 2800 POWDER MILL RD ADELPHI MD 20783-1197
1	DIRECTOR US ARMY RSCH LABORATORY ATTN AMSRL CI LL TECH LIB 2800 POWDER MILL RD ADELPHI MD 207830-1197
1	DIRECTOR US ARMY RSCH LABORATORY ATTN AMSRL D D SMITH 2800 POWDER MILL RD ADELPHI MD 20783-1197
1	HQDA DAMO FDT 400 ARMY PENTAGON WASHINGTON DC 20310-0460
1	DPTY CG FOR RDA US ARMY MATERIEL CMD AMCRDA 5001 EISENHOWER AVE ALEXANDRIA VA 22333-0001
1	INST FOR ADVNCD TCHNLGY THE UNIV OF TEXAS AT AUSTIN PO BOX 202797 AUSTIN TX 78720-2797
1	DARPA 3701 N FAIRFAX DR ARLINGTON VA 22203-1714
1	NAVAL SURFACE WARFARE CTR CODE B07 J PENNELLA 17320 DAHLGREN RD BLDG 1470 RM 1101 DAHLGREN VA 22448-5100

NO. OF
COPIES ORGANIZATION

1	US MILITARY ACADEMY MATH SCI CTR OF EXCELLENCE MADN MATH MAJ HUBER THAYER HALL WEST POINT NY 10996-1786
10	W L GORE AND ASSOC ATTN S MACKENZIE (5 CYS) DR N BECK TAN (5 CYS) 201 AIRPORT ROAD ELKTON MD 21922
4	UNIV OF DELAWARE ATTN PROF R MCCULLOUGH (2 CYS) PROF JOHN OLSON (2 CYS) COLBURN LABORATORY DEPT OF CHEMICAL ENGINEERING NEWARK DE 19716

ABERDEEN PROVING GROUND

2	DIRECTOR US ARMY RSCH LABORATORY ATTN AMSRL CI LP (TECH LIB) BLDG 305 APG AA
5	DIRECTOR US ARMY RSCH LABORATORY ATTN AMSRL WM MA T MULKERN BLDG 4600

ABSTRACT ONLY

1	DIRECTOR US ARMY RSCH LABORATORY ATTN AMSRL CI AP TECH PUBS 2800 POWDER MILL RD ADELPHI MD 20783-1197

39

INTENTIONALLY LEFT BLANK

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE March 2001	3. REPORT TYPE AND DATES COVERED Final

4. TITLE AND SUBTITLE

Material Properties of Bi-Modal Epoxy Networks

5. FUNDING NUMBERS

PR: 1L162618AH80

6. AUTHOR(S)

MacKenzie, S.J. (U of DE); Mulkern, T.J.; Beck Tan, N.C. (both of ARL)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Research Laboratory
Weapons & Materials Research Directorate
Aberdeen Proving Ground, MD 21005-5066

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Laboratory
Weapons & Materials Research Directorate
Aberdeen Proving Ground, MD 21005-5066

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

ARL-TR-2413

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The necessity for epoxies in new technologies is overwhelming. For these epoxies to perform at their maximum capabilities, both high strength and toughness must be in the list of mechanical properties. This is where bi-modal networks become important. Their combinations of both long- and short-chain cross linkers vary the cross-link density of the epoxy and thus improve the toughness. Here, a study was done to see if these bi-modal networks increase toughness without loss in modulus. Through the use of the differential scanning calorimeter to find the glass transition temperature, the dynamic mechanical analyzer to find the storage modulus, and the Izod impact machine to find the impact strength, we can make a conclusion whether these networks really work. In the beginning, the results seemed to be what we had hoped for, that is, the decrease in cross-link density did improve the impact strength; however, the storage modulus also decreased with a decrease in cross-link density. Finally, the conclusion can be stated that the bi-modal network does increase the toughness of this system but with a loss in modulus.

14. SUBJECT TERMS

bi-modal network   impact strength
epoxy

15. NUMBER OF PAGES
47

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT